

Comparison of the X-ray Atomic Form Factors for Crystalline and Free-Atom Lithium

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Abstract

X-ray atomic form factors, f , have been calculated for crystalline and free-atom lithium using the same Gaussian-orbital basis and the same exchange-correlation potential in the local density approximation by the self-consistent linear combination of Gaussian orbitals (LCGO) method. The difference between f calculated for an Li crystal and f for free Li atoms is less than 0.8%, which is rather small. For free Li atoms the values of f deviate from those obtained by Hartree-Fock calculations by 1.5 to 3% for $\sin \theta/\lambda < 1.2 \text{ \AA}^{-1}$.

1. Introduction

The X-ray atomic form factor, f , is an important physical quantity for X-ray crystallography. Because of some difficulties with the accuracy of measurements, defects in samples and so on, complete experimental data for f are lacking. Usually, the theoretical values are used in practice. For a long time, it was difficult to calculate the charge distribution of electrons in a crystal, so the existing tables of X-ray atomic form factors were obtained from calculating the charge density for a free atom (Lonsdale, 1962; Cromer & Waber, 1974; Hubbell, Veicelle, Briggs, Brown, Cromer & Howerton, 1975). It is generally agreed that the effect of redistribution of electrons on f can be ignored as free atoms combine into a crystal (see, for example, Kittel, 1976).

Recently, following improvements in experimental equipment and developments in the theory of solid-state physics, many workers have shown that the idea stated above is unreliable. At small values of $\sin \theta/\lambda$, the experimental results for f for Al, Cu and Fe crystals are clearly less than the values calculated for corresponding free atoms by the Hartree-Fock (HF) method (Batterman, Chipman & Demarco, 1961; Jennings, Chipman & Demarco, 1964). Rath & Callaway (1973) calculated the values of f for a Cr crystal. Their results are less than the values calculated for the free Cr atom by the HF method, but are closer to the experimental data for a Cr crystal. Schneider, Hansen & Kretschmer (1981) systematically collected a variety of data on f for Cu, including both experimental and theoretical results. It follows from these data that, in general, the calculated values of f for the free Cu atom are larger than those for a Cu crystal, and the latter values are closer to the experimental

results for a Cu crystal. These data also show obvious diversity among the calculated values, obtained by different authors using different methods.

Both crystal and free atom are many-electron systems, so that approximation methods must be employed. It is noteworthy that, when comparing the X-ray atomic form factor calculated for a crystal with that for a free atom, the error caused by using different approximation methods should be avoided.

To answer the question of whether the X-ray atomic form factor of a crystal agrees with that for free atoms, it is necessary to investigate various elements. The present work is devoted to the element lithium.

2. Method of calculation

The X-ray atomic form factor is given by

$$f(\mathbf{K}) = \int \rho(\mathbf{r}) \exp(i\mathbf{K} \cdot \mathbf{r}) d\mathbf{r}, \quad (1)$$

$$\mathbf{K} = 2\pi(\mathbf{s} - \mathbf{s}_0)/\lambda, \quad (2)$$

where $\rho(\mathbf{r})$ is the charge density of electrons, which can be obtained by solving the single-electron wave equation, λ is the X-ray wavelength, \mathbf{s} and \mathbf{s}_0 are the unit vectors in the direction of the incident and scattered beams, respectively. If the angle between \mathbf{s} and \mathbf{s}_0 is denoted by 2θ , then (2) is expressed as

$$K = (4\pi/\lambda) \sin \theta. \quad (3)$$

As a special case assume that the electronic cloud is spherically symmetric; then (1) becomes

$$f(K) = 4\pi \int_0^\infty \rho(r) [(\sin Kr)/Kr] r^2 dr. \quad (4)$$

In atomic units ($\hbar = 2m = e^2/2 = 1$) the single-electron wave equation for the system of a free atom can be written as

$$\hat{H}\psi_{n\sigma}(\mathbf{r}) = \varepsilon_{n\sigma}\psi_{n\sigma}(\mathbf{r}), \quad (5)$$

$$\hat{H} = -\nabla^2 + V_\sigma. \quad (6)$$

The potential V_σ , referring to the electronic spin σ , contains the Coulomb potential of the nucleus and that of the average distribution of electrons in the system, plus the exchange-correlation potential $V_{xc\sigma}$:

$$V_\sigma(\mathbf{r}) = -\frac{2Z}{r} + 2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\tau - V_{xc\sigma}(\rho_\sigma, \rho_{-\sigma}), \quad (7)$$

where Z is the atomic number, $\rho_\sigma(\rho_{-\sigma})$ is the charge

density of electrons with spin $\sigma(-\sigma)$, and we have

$$\rho(\mathbf{r}) = \sum_{\sigma} \rho_{\sigma}(\mathbf{r}) = \sum_{n\sigma}^{\text{occ.}} |\psi_{n\sigma}(\mathbf{r})|^2. \quad (8)$$

The single-electron wave function $\psi_{n\sigma}$ can be expanded in a set of basis functions

$$\psi_{n\sigma}(\mathbf{r}) = \sum_{i,j} C_{ni,j\sigma} u_{i,j} \chi_{\sigma}, \quad (9)$$

in which χ_{σ} is the spin wave function. We may choose a set of Gaussian orbitals as the basis set:

$$u_{i,j} = N_i r^i \exp(-\xi_i r^2) Y_{i,j}(\theta, \varphi), \quad (10)$$

where N_i is the normalization constant

$$N_i = [2(2\xi_i)^{i+3/2} / \Gamma(i+3/2)]^{1/2}. \quad (11)$$

ξ_i is the exponent of the i th Gaussian orbital, and $Y_{i,j}$ is the angular function which is a Kubic harmonic of order i , type j , normalized to unity (von der Lage & Bethe, 1947). In general, the spherical harmonic Y_{lm} is more suitable for a free-atom calculation, but to make the basis set for the free-atom calculation the same as that for the crystal calculation, we still use the Kubic harmonic here, as we did in previous papers.

From the above formulae, the charge density for a free atom of lithium was calculated. In this work, the exchange-correlation potential employed is that of Rajagopal (1979) which has the same functional form as that of von Barth & Hedin (1972), but with somewhat different parameters; the basis set used is the same as that employed in previous papers (Callaway, Zou & Bagayoko, 1982, 1983; Zou, 1984) and the configuration $(1s)^2(2s)^1$ is considered. Substitution of the calculated values of ρ into (1) gives the X-ray atomic form factors.

For a crystal system, in the local density approximation, the single-electron wave equation is

$$\hat{H}\psi_{n\sigma}(\mathbf{k}, \mathbf{r}) = \varepsilon_{n\sigma} \psi_{n\sigma}(\mathbf{k}, \mathbf{r}), \quad (12)$$

$$\hat{H} = -\nabla^2 - 2Z \sum_{\mu} \frac{1}{|\mathbf{r} - \mathbf{R}_{\mu}|} + 2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\tau - V_{\chi c\sigma}, \quad (13)$$

where \mathbf{R}_{μ} is any direct-lattice vector. In (13) the interaction of the considered electron with all nuclei and electrons in the crystal is included. The single-electron wavefunction $\psi_{n\sigma}(\mathbf{k}, \mathbf{r})$ refers to the state of wave vector \mathbf{k} in band n and spin σ . It obeys Bloch's theorem and can be expanded in a set of basis $\phi_i(\mathbf{k}, \mathbf{r})$:

$$\psi_{n\sigma}(\mathbf{k}, \mathbf{r}) = \sum_i C_{ni}(\mathbf{k}, \sigma) \phi_i(\mathbf{k}, \mathbf{r}) \chi_{\sigma}. \quad (14)$$

To satisfy Bloch's theorem, ϕ_i is constructed as properly phased linear combinations of Gaussian orbitals u_i placed on the lattice sites:

$$\phi_i(\mathbf{k}, \mathbf{r}) = N^{-1/2} \sum_{\mu} \exp(i\mathbf{k} \cdot \mathbf{R}_{\mu}) u_i(\mathbf{r} - \mathbf{R}_{\mu}), \quad (15)$$

where N is the number of unit cells in the crystal.

In the calculation for the Li crystal, the exchange-correlation potential and basis set are the same as those used in the calculation for the free Li atom and the b.c.c. structure was considered. When (12) is solved using (8), the charge density for the Li crystal is obtained. By a Fourier transformation, $\rho(\mathbf{K})$, the Fourier coefficient of $\rho(\mathbf{r})$, is generated. It is convenient to calculate f in this way. Note that

$$\rho(\mathbf{K}) = (1/\Omega) \int \rho(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}) d\tau \quad (16)$$

and

$$\rho(0) = (1/\Omega) \int \rho(\mathbf{r}) d\tau = Z/\Omega, \quad (17)$$

where Ω is the volume of the unit cell. Thus, (1) is simplified as

$$f(\mathbf{K}) = Z\rho(\mathbf{K})/\rho(0). \quad (18)$$

3. Results and discussion

Our calculated results for the X-ray atomic form factors of Li, f_a (for the free atom) and f_c (for the crystal), are shown in Table 1 and Fig. 1, together with f_a by a HF calculation (Cromer & Waber, 1974). In Table 1, the numerical results are listed for the reflections with $\sin \theta/\lambda < 1.2 \text{ \AA}^{-1}$. To show all the data, Fig. 1 gives a plot of f_a calculated as a function of $\sin \theta/\lambda$ for a large range of reflections. On such a scale the plot is not clear enough to distinguish the values calculated in the three cases stated above. For comparison of these three cases, an enlarged plot is included in Fig. 1. From Table 1 and Fig. 1, the following points are obtained:

(1) For lithium the differences between f_c and f_a , calculated by using the same basis set and potential, are less than 0.8%. This difference is rather small. So it is not unreasonable to regard f_a , calculated for a free Li atom, as the value of the X-ray atomic form factor for an Li crystal.

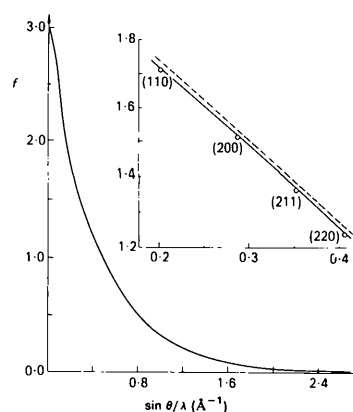


Fig. 1. X-ray atomic form factors for lithium. The solid line and hollow circles are the present results for the free atom and crystal, respectively. The dashed line is the Hartree-Fock result.

Table 1. *The calculated X-ray form factors of lithium for $\sin \theta/\lambda < 1.2 \text{ \AA}^{-1}$*

f_c and f_a represent the values for an Li crystal and a free Li atom, respectively. The Hartree-Fock values f_a^{HF} for a free Li atom are also given.

| K | $\sin \theta/\lambda$ (\AA^{-1}) | f_c | f_a | f_a^{HF} |
|-----|--|-------|-------|-------------------|
| 110 | 0.203 | 1.710 | 1.715 | 1.735 |
| 200 | 0.286 | 1.515 | 1.518 | 1.532 |
| 211 | 0.351 | 1.368 | 1.372 | 1.382 |
| 220 | 0.405 | 1.234 | 1.238 | 1.251 |
| 310 | 0.453 | 1.116 | 1.120 | 1.135 |
| 222 | 0.496 | 1.017 | 1.020 | 1.035 |
| 321 | 0.536 | 0.927 | 0.932 | 0.948 |
| 400 | 0.573 | 0.854 | 0.856 | 0.870 |
| 330 | 0.608 | 0.787 | 0.791 | 0.804 |
| 411 | 0.608 | 0.787 | 0.791 | 0.804 |
| 420 | 0.641 | 0.728 | 0.734 | 0.748 |
| 332 | 0.672 | 0.676 | 0.682 | 0.696 |
| 422 | 0.702 | 0.631 | 0.634 | 0.648 |
| 431 | 0.730 | 0.587 | 0.592 | 0.604 |
| 510 | 0.730 | 0.587 | 0.592 | 0.604 |
| 521 | 0.785 | 0.517 | 0.521 | 0.529 |
| 440 | 0.810 | 0.485 | 0.488 | 0.500 |
| 433 | 0.834 | 0.456 | 0.461 | 0.472 |
| 530 | 0.834 | 0.456 | 0.461 | 0.472 |
| 600 | 0.859 | 0.431 | 0.435 | 0.445 |
| 444 | 0.992 | 0.314 | 0.315 | 0.326 |
| 550 | 1.013 | 0.310 | 0.312 | 0.313 |
| 732 | 1.128 | 0.232 | 0.233 | 0.234 |

(2) If the two sets of results calculated for the free Li atom are compared, it can be seen that $f_a(\mathbf{K})$ is less than $f_a^{\text{HF}}(\mathbf{K})$. In general, the difference $f_a^{\text{HF}}(\mathbf{K}) - f_a(\mathbf{K})$ covers a range from 1.5 to 3% for $\sin \theta/\lambda < 1.2 \text{ \AA}^{-1}$. The major part of the deviation of those values calculated using the local density approximation from HF atomic form factors is due to the self-interaction error (Perdew & Zunger, 1981). Moreover, electron correlation effects are also important, particularly for low- Z elements (Hubbell *et al.*, 1975). It is conceivable that a part of the deviation is due to neglect of correlation effects in HF calculation.

(3) The discrepancy between $f_a(\mathbf{K})$ and $f_a^{\text{HF}}(\mathbf{K})$ is clearly larger than that between $f_a(\mathbf{K})$ and $f_c(\mathbf{K})$. This means that the discrepancy arising from the use of different methods is large enough to exceed that existing between the free Li atom and the Li crystal. In order to compare the X-ray atomic form factors for a free Li atom and an Li crystal, the same method should be used. That is, the basis set and potential

should be the same in calculating electronic charge density for both free atom and crystal.

(4) The data for f_c in Table 1 and Fig. 1 are calculated with lattice spacing $a = 6.597 \text{ a.u.}$ (*i.e.* 3.491 \AA) which is the experimental lattice constant of Li. To check the influence of lattice spacing on f_c , a series of calculations with $a = 5.8, 6.2, 6.5, 6.8$ and 8.0 a.u. were carried out. The results show that the differences among $f_c(\mathbf{K})$ calculated with these lattice spacings are less than 0.6%.

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